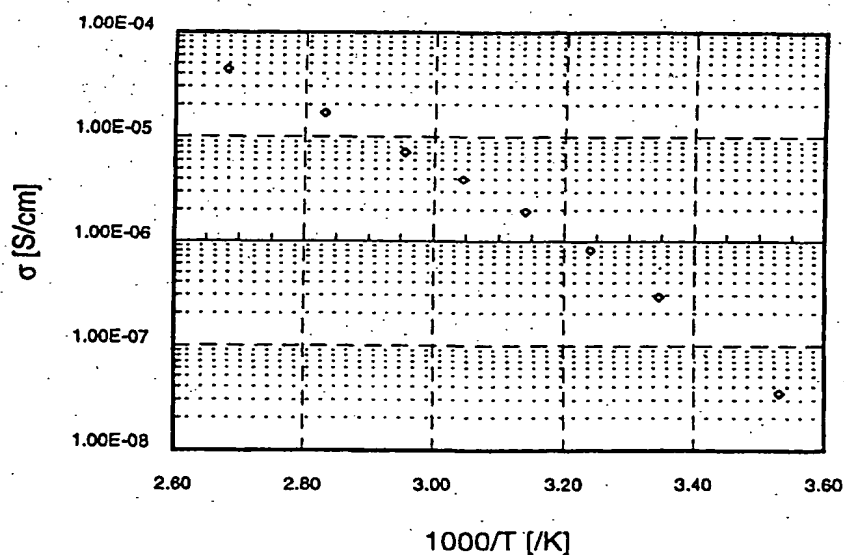




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : H01M 6/18, 6/24, 10/08		A1	(11) International Publication Number: <b>WO 00/05774</b>
			(43) International Publication Date: 3 February 2000 (03.02.00)
(21) International Application Number: PCT/US99/16760		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 23 July 1999 (23.07.99)			
(30) Priority Data: 60/093,907 23 July 1998 (23.07.98) US			
(71) Applicant: MASSACHUSETTS INSTITUTE OF TECHNOLOGY [US/US]; 77 Massachusetts Avenue, Cambridge, MA 02139 (US).			
(72) Inventors: MAYES, Anne, M.; 75 Trapelo Road, Waltham, MA 02154 (US). SADOWAY, Donald, R.; 75 Trapelo Road, Waltham, MA 02154 (US). BANERJEE, Pallab; Apt. 205, 1575 Tremont Street, Boston, MA 02120 (US). SOO, Philip; Apt. 143E, 550 Memorial Drive, Cambridge, MA 02139 (US). HUANG, Biying; Apt. 3, 6 Alberta Terrace, Cambridge, MA 02140 (US).		Published With international search report.	
(74) Agent: SCOZZAFAVA, Mary, Rose; Clark & Elbing LLP, 176 Federal Street, Boston, MA 02110-2214 (US).			

(54) Title: BLOCK COPOLYMER ELECTROLYTE

Ionic conductivity of SDBCE ([EO]:Li<sup>+</sup>~9:1)

## (57) Abstract

A polymer electrolyte (30) includes a microphase separated block copolymer including at least one ionically conductive block (32) and at least one second block (34) that is immiscible in the ionically conductive block, an anion (36) immobilized on the polymer electrolyte and a cationic species. The ionically conductive block provides a continuous ionically conductive pathway through the electrolyte. The electrolyte may be used as an electrolyte in an electrochemical cell (20) or as a conductive binder in a cathode (22) or anode (24).

## BLOCK COPOLYMER ELECTROLYTE

### Field of the Invention

5           This invention relates to phase separated block copolymers useful as a polymer electrolyte in a battery.

### Background of the Invention

Rechargeable batteries enjoy an enormous and constantly growing global market due to the increased use of portable consumer electronic  
10   products. The lithium solid polymer electrolyte battery is an attractive rechargeable battery technology due to its high predicted energy density and low associated materials and processing costs. A successful lithium battery requires the use of an electrolyte that is highly conductive in order to sustain a high density.

15           Contemporary rechargeable lithium ion batteries utilize a liquid electrolyte and are assembled with a physical separator layer between the anode and the cathode to prevent electrical shorting. The use of a physical separator results in increased costs, due to associated materials and processing. In addition, contemporary liquid electrolytes are volatile at elevated temperatures,  
20   exhibit electrochemical breakdown at voltages ( $\sim 4.5V$ ) that fail to fully exhibit cathode capacity, and can react chemically with electrode components. This limits both the (total available charge) and the maximum current density and reduces the useful cycle life (number of charge/discharge cycles to failure).

25           In order to overcome the limitations inherent in liquid electrolytes, solid polymer electrolytes have been developed in which ion mobility is possible through coordination of the lithium ion with suitable sites on the polymer chain. An inherent inverse relationship between ionic conductivity and dimensional stability exists in most known polymer electrolytes. Prior art

-3-

distinct chemical species that are covalently linked. The chemical connectivity of the blocks results in unique thermodynamic and rheological behavior. At high temperatures or in a common solvent, block copolymers form homogenous phases in which the different blocks are segmentally mixed.

5 Upon lowering the temperature or concentrating the polymer by solvent evaporation, the repulsion between unlike segments increases causing the copolymer to phase separate locally into domains rich in one or the other of the block components. These domains form ordered nanostructures, the morphology of which is governed by the relative volume fraction of the two

10 blocks. The microphase separation process imparts dimensional stability to the material, even for materials in which both blocks individually are inherently amorphous and at temperatures exceeding the glass transition temperature of both blocks.

Published International Application WO 98/16960 describes a solid

15 polymer electrolyte block copolymer that includes an ionically conductive polymer. A continuous lithium ion conducting pathway was obtained. However, the practical cell current is undesirably low. This is attributed to the low transference number for lithium ions in this system ( $t_{Li} \approx 0.3 - 0.5$ ). Stated differently, anionic migration during use may result in a salt concentration

20 gradient in the electrolyte. Anions are attracted to the positive electrode (cathode) causing salt depletion from the electrolyte interior. Such a concentration gradient impedes the movement of the lithium ions between the electrodes, resulting in prolonged and undesirable polarization of the cell.

Significant efforts have been directed toward viable solid polymer

25 electrolytes, yet improvements are greatly needed.

It is an object of the present invention to provide an electrolyte for use in batteries that exhibits good ionic conductivity while retaining good

-5-

embodiment of the invention, the anion is immobilized on the second block of copolymer.

By "microphase separated" as that term is used herein, it is meant that the block copolymer has been subjected to conditions that favor the association of the copolymer chain to form regions or domains within the copolymer containing substantially only a single selected block. The blocks of a microphase separated block copolymer therefore are locally segregated into order domains.

In a preferred embodiment, the microphase separated copolymer blocks are non-glassy and amorphous throughout the temperature range of use, and the mobile cationic species is substantially localized in the ionically conductive block. The cationic species includes lithium, sodium, potassium, magnesium and calcium. In a preferred embodiment of the invention, the anion exhibits delocalized charge density.

The ionically conductive block may include a polymer backbone having polyalkylene oxide or polyalkylene glycol side chains. The polyalkylene oxide or polyalkylene glycol side chains may be of a length less than about 20 oxide units. A preferred polyalkylene oxide is polyethylene oxide. The volume fraction of the ionically conductive block is in the range of about 0.50 to about 0.85.

In one preferred embodiments, the second polymer block is made up of a copolymer comprised of a first monomer selected for its ability to microphase separate from the ionically conductive block and a second monomer comprising an anion or neutral precursor thereof. In other preferred embodiments, the ionically conductive block is made up of a copolymer comprised of a first ionically conductive monomer and a second monomer comprising an anion or neutral precursor thereof. The neutral precursor is

-7-

components are in direct physical contact with each other or when components communicate via intermediate structures which are capable of transporting the ion of interest.

The term "electronic communication" is used to indicate a relationship between components of a battery whereby electrons are capable of movement or flow with little or no resistance, i.e., under the driving force normally encountered in the operation of a battery.

#### Brief Description of the Drawing

The invention is described with reference to the following Figures, which are intended to be illustrative of the invention only and which are in no way intended to be limiting of the invention and in which:

Figure 1 is a schematic illustration of a typical lithium battery cell;

Figure 2 is a schematic illustration of a polymer electrolyte according to the present invention;

Figure 3 shows the temperature dependence of the electrical conductivity of a 1:1:1 self-doped block copolymer electrolyte (SDBCE) prepared according to Example 1; and

Figure 4 shows the electrical conductivity of a 1:1:1 self-doped block copolymer electrolyte including addition of polyethyleneglycol dimethylether (PEGDME) prepared according to the example;

Figure 5 is a plot of the temperature-dependence of the electrical conductivity for an unlithiated 3:1:2 block copolymer precursor and a lithated 3:1:2 self-doped block copolymer electrolyte, including polyethyleneglycol dimethylether (PEGDME);

Figure 6 is a schematic illustration of a cell configuration used in battery charge/discharge testing;

-9-

between the battery's cathode 22 and anode 24 which causes the lithium ions and electrons to be withdrawn from lithium hosts 26 at the battery cathode 22. Lithium ions flow from the cathode 22 to the battery anode 24 through a polymer electrolyte 28 to be reduced at the anode 24. The process requires  
5 energy. During subsequent discharge, lithium ions and electrons re-enter lithium hosts at the cathode 22 while lithium is oxidized to lithium ions at the anode, an energetically favorable process that drives electrons through a load in an external circuit, providing electrical power.

A solid polymer electrolyte based on the microphase separation of  
10 two chemically distinct polymer chains into ionically conducting and secondary domains is set forth in the published International Application WO 98/16960. The block copolymer of WO 98/16960 consists of two non-glassy, amorphous polymers, one of which is capable for solubilizing a lithium salt. While the material has been demonstrated to conduct lithium ions as an electrolyte and as  
15 a binder in the cathode, the maximum sustainable current of cells into which the electrolyte has been incorporated is disappointingly low. This may be attributed in part to the low transference number of the lithium cation.

During battery operation, anions also move; however, their movement is not productive to the faradaic process of the electrochemical cell.  
20 Due to their negative charge, the anions move to the positive electrode (the cathode) resulting in a salt concentration gradient which is an impediment to the faradaic process, as the lithium cations cannot traverse the electrolyte easily. This effect is reflected in the low lithium ion transference value ( $t_{Li}$ ) of the electrolyte of around 0.3-0.5. Where the current is borne by a single ionic  
25 species in solution, that ionic species is said to have a transference number of 1.0.

The transference number of the lithium cation in an electrolyte

-11-

Secondly, higher  $t_{Li}$  translates into a lower kinetic barrier to  $Li^+$  removal from the cathode when the cell is recharging. The barrier is the result of an accumulation of anions from the electrolyte salt dopant at the electrode/electrolyte interface.

5           In addition, the mobility of the cation may be improved by reducing the charge density of the anion. When the charge of anion is concentrated in a small area, i.e., on a single atom, the anion acts as a point charge which may be strongly attractive to the cation. On the other hand, if the charge of the anion is delocalized over a larger physical area, the attractive force of the anion is  
10       diminished at any given location in the electrolyte. Thus, the mobility of the cation may be further enhanced by reducing the charge density of the anion. Charge density may be diffused over a larger physical region in a variety of ways. For example, an anion of large atomic radius may be used, such as iodide. Alternatively, the anion may be multiatomic and the charge may be  
15       delocalized over the entire species, such as a carboxylate  $CO_2^-$  or sulfonate group.

          According to the invention, an electrolyte that exhibits improved mobility of current carrying cation is provided. The polymer electrolyte having a cationic species is prepared from a block copolymer of at least one ionically  
20       conductive block and at least one second block. Anions of the electrolyte are immobilized on the block copolymer. Upon microphase separation, nanoscale domains are formed alternately rich in the ionically conductive and second copolymer blocks. The composition is selected so that ionically conductive permit the free movement of the mobile cationic species throughout the  
25       material. By attachment of the anion to the polymer electrolyte, a high molecular weight "macroanion" is formed. The mobility of the macroanion is low and the transference value of the mobile cation species is enhanced. The

-13-

including at least one ionically conductive block 32 and at least one second block 34 and having an immobilized anion 36. The ionically conductive block and the second block are selected such that a phase separated block copolymer is formed. The block copolymer solid electrolyte of the invention may be a  
5 diblock copolymer, triblock copolymer and the like.

The ionically conductive block 32 is comprised of one or more highly electronegative oxygen-containing species, such as alkyl ethers, in which small monovalent and divalent cations are known to be solubilized. Preferred ionically conductive blocks include polymer chains derivatized with  
10 polyethylene oxide (PEO), polyethylene glycol (PEG), polypropylene oxide (PPO) and/or polypropylene glycol (PPG). The ionically conductive block may be, but is not limited to, methoxy PEG methacrylate (referred to herein as POEM), methoxy PEG acrylate and other acrylate and polymers modified to include short PEO, PEG, PPO or PPG side chains, polybutadiene modified to  
15 include PEO, PEG, PPO, or PPG side chains or polystyrene similarly modified to include alkylether side chains. The number of alkylene oxide units of the side chain is selected to provide a high ionic conductivity. The side chains may include up to about 20 alkylene oxide units each. Ethylene oxide is a preferred alkylene oxide. In selecting the ionically conductive block polymer, it is  
20 helpful to keep in mind the fact that longer side chains may exhibit higher degrees of crystallinity. The ionically-conductive block also can be defined by ionically-conductive polymeric material such that described Ward et al. In U.S. Patent No. 5,051,211, incorporated herein by reference. In preferred  
embodiments, the polymer block is selected so that the glass transition  
25 temperature of the block is less than service temperature and selected such that crystallization does not occur.

The second block is so as to be immiscible with the ionically



-15-

than its anionic derivative. For example, the neutral species may be a carboxylic acid that can be neutralized, for example by addition of lithium or sodium methoxide, to produce the corresponding lithium carboxylate salt, or an ester that can be hydrolyzed to produce the corresponding carboxylate salt.

5 Alternatively, the anion may be introduced into the copolymer as a charged species, such as a sulfonate or a phosphate. The cation in either embodiment may be the mobile cationic species of the electrolytic cell. Alternatively, the cation may be one which is amenable to block copolymer synthesis but which may be replaced by the mobile species in a separate step. For example,  $\text{Na}^+$   
10 may be replaced by  $\text{Li}^+$  in an ion exchange reaction.

An additional advantage of the immobilized anionic block copolymer of the invention is its increased electrochemical stability. Conventional electrolyte salts are subject to electrochemical breakdown at voltages (4.5V) that fail to exploit the full capacity of the cathode. A self-doped block  
15 copolymer electrolyte is not expected to be subject to electrochemical breakdown at the same voltages as a conventional electrolyte salt with its macroanion character. Thus, the self-doped block copolymer electrolyte allows for the possibility of a high voltage battery and hence a higher energy density. In addition, selection of a counteranion is not limited to those that have high  
20 electrochemical breakdown voltages. Virtually any anion capable of incorporation into the block copolymer of the invention is contemplated as within the scope of the invention.

Each of the ionically-conductive and anion-immobilizing blocks can be a mixture of components, that is, each block can be, for example, a random  
25 copolymer of different components so long as one block is sufficiently ionically conductive and so long as the material as a whole has sufficient dimensional stability at use temperatures. A block copolymer in which one

-17-

mobile cation for the ionically conductive domains is a function of the number of cation solvating units (typically ethylene oxide or EO) present in the ionically conducting block. The minimum level is not known; however, significant conductivities have been observed with Li:EO ratios in the range of about 1:9 to about 1:27. *See*, Figures 3 through 6 and the Examples herein below.

The continuous ionically-conductive domains define a continuous pathway when the block copolymer is ordered either due to defects in the association of the polymer chains to form the domains or the inherent morphology of the microphase separated block copolymer. Thus, for example, the polymer electrolyte blocks may phase separate locally to form cylindrical or spherical ordered phases in which the ionically-conductive domain forms the continuous matrix phase. Bicontinuous periodic block copolymer morphologies such as a double gyroid arrangement, double diamond configuration or the like can be used. Alternatively, the polymer electrolyte may phase separate into a lamellar (layered) structure. Such a layered structure may or may not form a phase which provides a continuous pathway through the electrolyte between the cathode and the anode (dependent upon the orientation of the lamella). In such cases a continuous phase may nonetheless be formed by introduction of morphological defects to provide a topologically connected continuous ionically-conductive pathway. These structures are known to those of ordinary skill in the art.

Compositions for forming the microphase separated block copolymer electrolyte may be selected so that the ionically-conductive blocks form continuous, ionically-conducting domains upon microphase separation. In one preferred embodiment, both blocks are amorphous, rheologically in a rubbery or melt state, i.e., well above the glass transition temperature  $T_g$ , and non-

-19-

(bis(trifluoromethanesulfonyl) carbide),  $\text{CF}_3\text{CO}_2^-$ , and the like. The choice of cation is governed by the faradaic process of the electrodes, e.g.,  $\text{Li}^+$  for a lithium battery,  $\text{Na}^+$  for a sodium battery, etc. Lithium ion is a preferred cation.

In other preferred embodiments, it may be desired to add a  
5 conductive liquid to the solid polymer electrolyte. The conductive liquid desirably increases the conductivity of the mobile cationic species in the ionically conductive block without substantial deleterious effect to the mechanical integrity or dimensional stability of the block copolymer. Suitable liquid conductors include, but are not limited to, oligomeric PEO or  
10 polyethylene glycol dimethyl ether. The lower molecular weight oligomer segregates preferentially into the ionically-conductive domain of the block copolymer, thereby improving the conductivity of the copolymer.

A self-doped block polymer electrolyte may be prepared as follows. Anionic synthesis is well-suited for the preparation of block copolymeric  
15 electrolytes with well-defined molecular weights and compositions. For example, the polymerization of methoxypolyethyleneglycol methacrylate (POEM; available from Polysciences) can be initiated anionically to yield to a polymer with a  $T_g$  of  $-60^\circ\text{C}$ . Diblock copolymers of POEM and lauryl methacrylate can be prepared by sequential addition of lauryl methacrylate to  
20 living POEM homopolymer. Alternatively, block copolymers can be prepared by reaction of end-functionalized homopolymers, by addition polymerization of one block component onto an end-functionalized homopolymer, or by sequential addition of two monospecies in a living free radical polymerization, or atom transfer radical polymerization.

25 In instances where a neutral precursor of the anionic species has been used in synthesis, the anionic species may be generated after formation of the block copolymer or after polymerization is complete.

-21-

again over 25% trioctylaluminum/hexane solution.

The block copolymer was polymerized at  $-78^{\circ}\text{C}$  by the sequential addition of a mixture of purified lauryl methacrylate (LMA, Aldrich) and *tert*-butyl methacrylate (Polysciences), followed by oligooxyethylene methacrylate (OEM, Aldrich, 9 ethylene oxides per repeat unit), to diphenylmethyl  
5 potassium initiator in 350 mL THF. Upon termination of the reaction with degassed methanol, the copolymer solution was concentrated on a rotary evaporator, precipitated in petroleum ether and finally centrifuged to isolate the colorless polymer. The polymer included a 1:1:1 molar ratio of the three  
10 monomer components and is referred herein as a 1:1:1 SDBCE.

On the basis of molar content of *tert*-butyl methacrylate in the block copolymer, a slight stoichiometric excess of *p*-toluenesulfonic acid was added to a 2 vol% block copolymer solution in toluene in order to hydrolyze the methacrylate functional group. The solution was refluxed at  $90^{\circ}\text{C}$  for 5 hours,  
15 during which time the *tert*-butyl ligand was replaced by a hydroxy group, thereby forming a methacrylic acid (MAA) repeat unit. Following hydrolysis, the block copolymer was precipitated out of solution, whereupon it was separated by filtration and dried in a vacuum oven for 48 hours at  $60^{\circ}\text{C}$ .

The final step in the preparation of the self-doped block copolymer electrolyte involved lithiation of the methacrylic acid groups by neutralization  
20 with a suitable base, lithium methoxide. This was accomplished by first drying the hydrolyzed polymer by repeated azeotropic distillation and drying over benzene. Toluene was then transferred into the reactor by cannula to form a 5 wt% solution. Finally, a stoichiometric amount of lithium methoxide was then  
25 injected into a small amount (2-3 mL) of polymer solution. Because the presence of methanol induces back-reaction of the lithiated carboxylate, a vacuum line was used to continuously remove methanol as it evolved in the

-23-

Figure 3 demonstrates that the self-doped block copolymer of the invention possessed acceptable conductivity, particularly at elevated temperatures. This establishes that lithium cations are localized in the ionically conductive domains, even though the anions are microphase separated into the second block domains.

Figure 4 shows the effect of introduction of additional conductive liquids on the conductivity of the electrolyte of the invention. The PEGDME is presumed to localize in the ionically conductive block domains. This has the effect of increasing the conductivity of the polymer without degrading the mechanical properties (the material does not flow). The increased conductivity may be due to the reduced crystallinity of the polymer at room temperature or the increased number of EO units in the ionically conductive domains, or both.

Example 2. This example describes the synthesis of an LMA-r-lithium methacrylate (LiMA)-b-POEM block copolymer electrolyte having a 3:1:2 molar ratio of LMA:LiMA:POEM. The different monomer proportions provided a block copolymer having an EO:Li ratio approaching 20, which is the nominal ratio for conventional PEO electrolytes.

*Synthesis.* The precursor of materials used in this study was first prepared using anionic methods. These methods were similar to those used in Example 1.

Following the isolation of the polymer by reverse precipitation from ethyl acetate and hydrolysis of the methacrylic acid *t*-butyl functional group, the material was precipitated from solution, filtered and dried. The material then was lithiated in toluene solution by dropwise addition of lithium methoxide (in 1 M methanol solution) under strictly airless and moisture-free conditions. A two-fold molar excess of lithium methoxide was used, and methanol was continuously removed to minimize back reaction. The excess

-25-

lithium according to the following half-reactions:

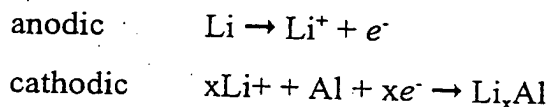


Figure 7 shows the first charge-discharge cycle of the test cell at a constant current density of  $0.5 \mu\text{A}/\text{cm}^2$ . The double plateau at 0.75 and 0 V vs.  $\text{Li}/\text{Li}^+$  is consistent with previous studies using this electrode, and confirms that lithium ions are being effectively transported to and from the aluminum. The discharge plateau was wider than the charge plateau, however, indicating some degree of irreversible capacity.

To determine whether this material is an effective single ion conductor The lithium transference number of the 3:1:2 block copolymer electrolyte with PEGDME was measured by step potential chronoamperometry. This was accomplished using a symmetric  $\text{Li}/\text{SDBCE}/\text{Li}$  cell configuration, which was constructed similarly to the cell in Figure 6. In this experiment, a 55 mV potential step was applied and current was recorded as a function of time. Because only current due to lithium ion transport is sustainable in this cell at long times, the transference number can be derived from the ratio  $i_\infty/i_0$ , where  $i_\infty$  is the limiting current plateau and  $i_0$  is the instantaneous current at  $t=0$ . The current profile shown in Figure 8 was obtained, corresponding to  $t_{\text{Li}^+}=0.88$ . Some limited anion mobility was observed, likely the result of small ion impurities in the electrolyte. This might be remedied by better purification of the electrolyte.

Figure 10 shows the results of an experiment to determine the limits of electrochemical stability of the SDBCE. Linear sweep voltammetry was performed at room temperature on the material in a  $\text{Li}/\text{SDBCE}/\text{Pt}$  cell with lithium metal also

-27-

1. A polymer electrolyte, comprising:  
a microphase separated block copolymer comprising at least one  
ionically conductive block and at least one second block that is immiscible in  
the ionically conductive block;  
5 an anion immobilized on the polymer electrolyte,  
wherein the ionically conductive block provides a continuous ionically  
conductive pathway through the electrolyte; and  
a cationic species.
2. The polymer electrolyte of claim 1, wherein the ionically  
10 conductive block and the second block are non-glassy and amorphous  
throughout a temperature range of use.
3. The polymer electrolyte of claim 1, wherein the anion is  
immobilized in the ionically conductive block.
- 15 4. The polymer electrolyte of claim 1, wherein the anion is  
immobilized in the second block.
5. The polymer electrolyte of claim 1, wherein the mobile cationic  
species is substantially confined in the ionically conductive block.
- 20 6. The polymer electrolyte of claim 1, wherein the cationic species  
is selected from the group consisting of lithium, sodium, potassium,  
magnesium and calcium.
7. The polymer electrolyte of claim 1, wherein the cationic species

-29-

13. The polymer electrolyte of claim 1, wherein the continuous ionically conductive pathway of the ionically conductive block is due to defects in microphase separation.

5 14. The polymer electrolyte of claim 1, wherein the volume fraction of the ionically conductive block is in the range of about 0.50 to about 0.85.

15 15. The polymer electrolyte of claim 1, wherein the second polymer block comprises a copolymer comprised of a first monomer selected for its ability to microphase separate from the ionically conductive block and a second monomer comprising an anion or neutral precursor thereof.

16. The polymer electrolyte of claim 1, wherein the ionically conductive block comprises a copolymer comprised of a first ionically conductive monomer and a second monomer comprising an anion or neutral precursor thereof.

15 17. The polymer of claim 15 or 16, wherein the copolymer is a random copolymer.

18. The polymer electrolyte of claim 1, wherein the amount of immobilized anion is selected to provide a specified anionic concentration in the electrolyte.

19. The polymer electrolyte of claim 1, wherein the second block is selected from the group consisting of polydecyl methacrylate, polylauryl



-31-

of the block copolymer chains of the ionically-conductive polymer is at least 100,000 Daltons.

26. The polymer electrolyte of claim 1, wherein the molecular weight of the block copolymer chains of the ionically-conductive polymer is at least 200,000 Daltons.

27. The polymer electrolyte of claim 1, further comprising a conductive liquid.

28. The polymer electrolyte of claim 25, wherein the conductive liquid is selected from the group consisting of oligomeric PEO and polyethylene glycol dimethyl ether.

29. The polymer electrolyte of claim 1, further comprising an electrolyte salt separate from the polymer electrolyte.

30. A polymer electrolyte comprising:  
a microphase separated block copolymer wherein a mobile cationic species is confined to a domain separate from an immobilized anionic species.

31. A block copolymer, comprising:  
at least one ionically conductive block;  
at least one second block that is immiscible in the ionically conductive block; and  
an anion immobilized on the polymer electrolyte.

-33-

one second block that is immiscible in the ionically conductive block;  
an anion immobilized on the polymer electrolyte,  
wherein the ionically conductive block provides continuous ionically  
conductive pathways through the electrolyte; and  
5 a faradaically active cationic species.

37. The cathode of claim 36, wherein the cation species is selected from the group consisting of lithium, sodium, potassium, magnesium and calcium.

38. An anode, comprising:  
10 an ionically conducting binder comprised of a microphase separated block copolymer comprising at least one ionically conductive block and at least one second block that is immiscible in the ionically conductive block;  
an anion immobilized on the polymer electrolyte,  
wherein the ionically conductive block provides continuous ionically  
15 conductive pathways through the electrolyte; and  
a faradaically active cationic species.

39. The polymer electrolyte of claim 7, wherein the electrolyte has a lithium ion transport value,  $t_{Li+}$ , of greater than 0.5.

40. The polymer electrolyte of claim 7, wherein the electrolyte has a  
20 lithium ion transport value,  $t_{Li+}$ , in the range of about 0.8 to 1.0.

41. The polymer electrolyte of claim 9, wherein the electrolyte comprises a lithium ion cationic species, and a ratio of alkylene oxide moiety to lithium ion is in the range of 9:1 to 16:1.

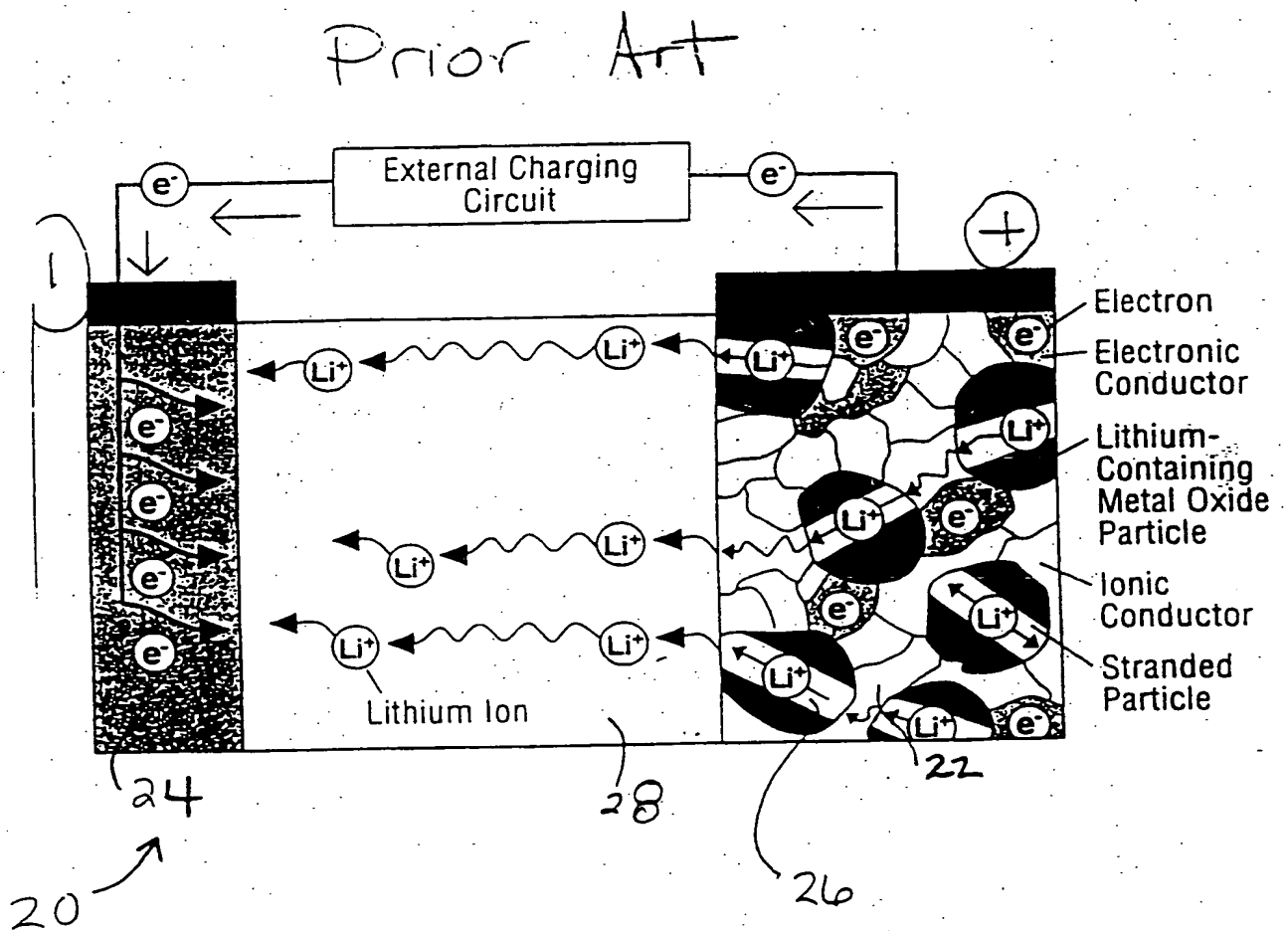


Figure 1

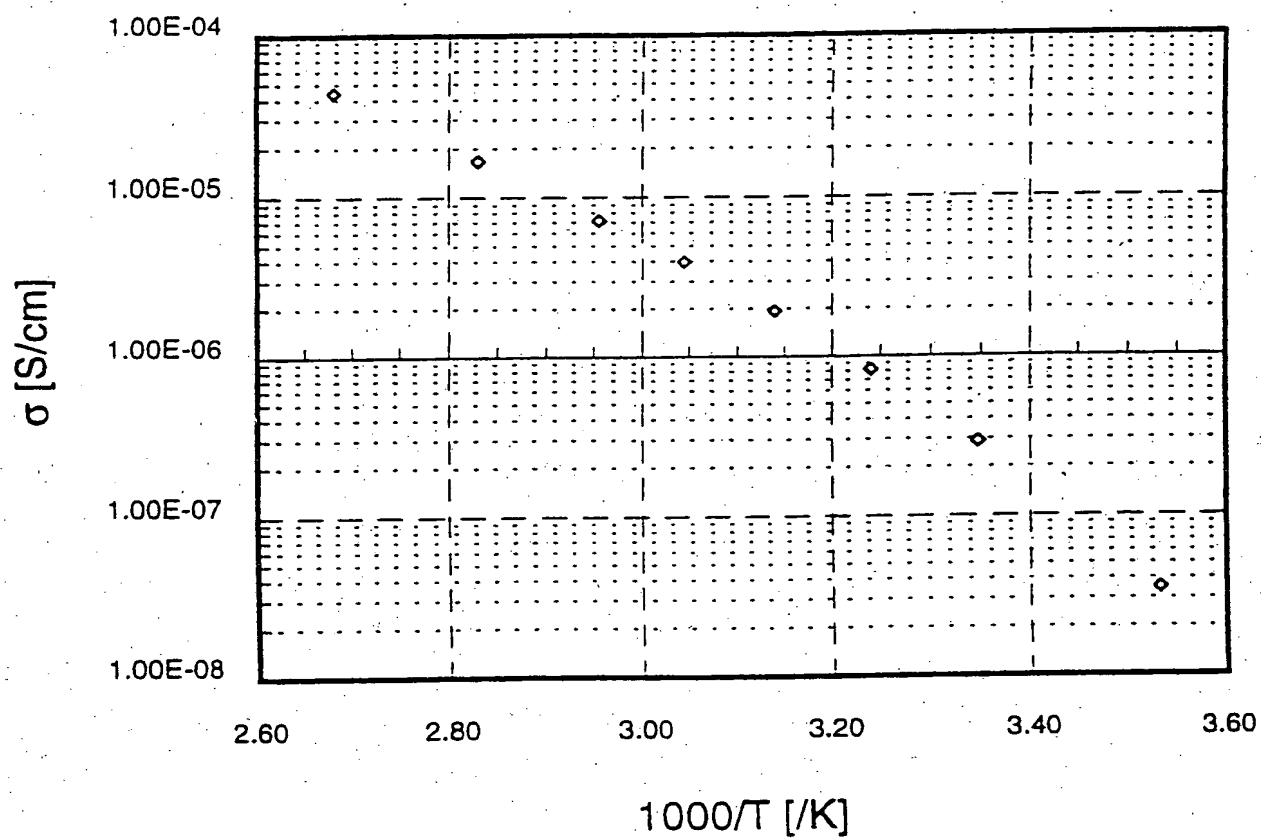
Ionic conductivity of SDBCE ([EO]:Li<sup>+</sup>~9:1)

Figure 3

13 July 1999

Figure 1. Electrical conductivity of the SDBCE (3:1:2) precursor and SDBCE (3:1:2) after lithiation.

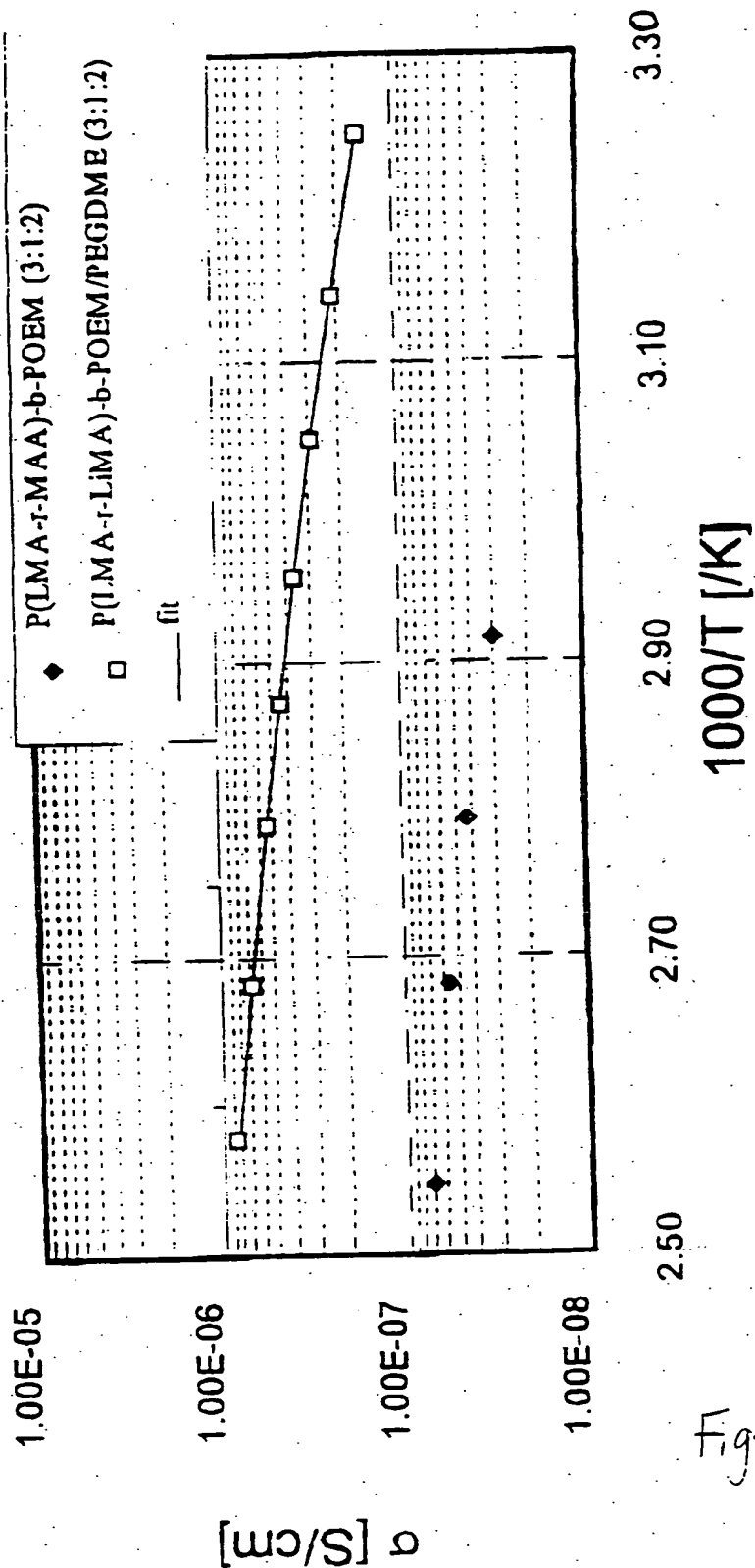


Figure 5

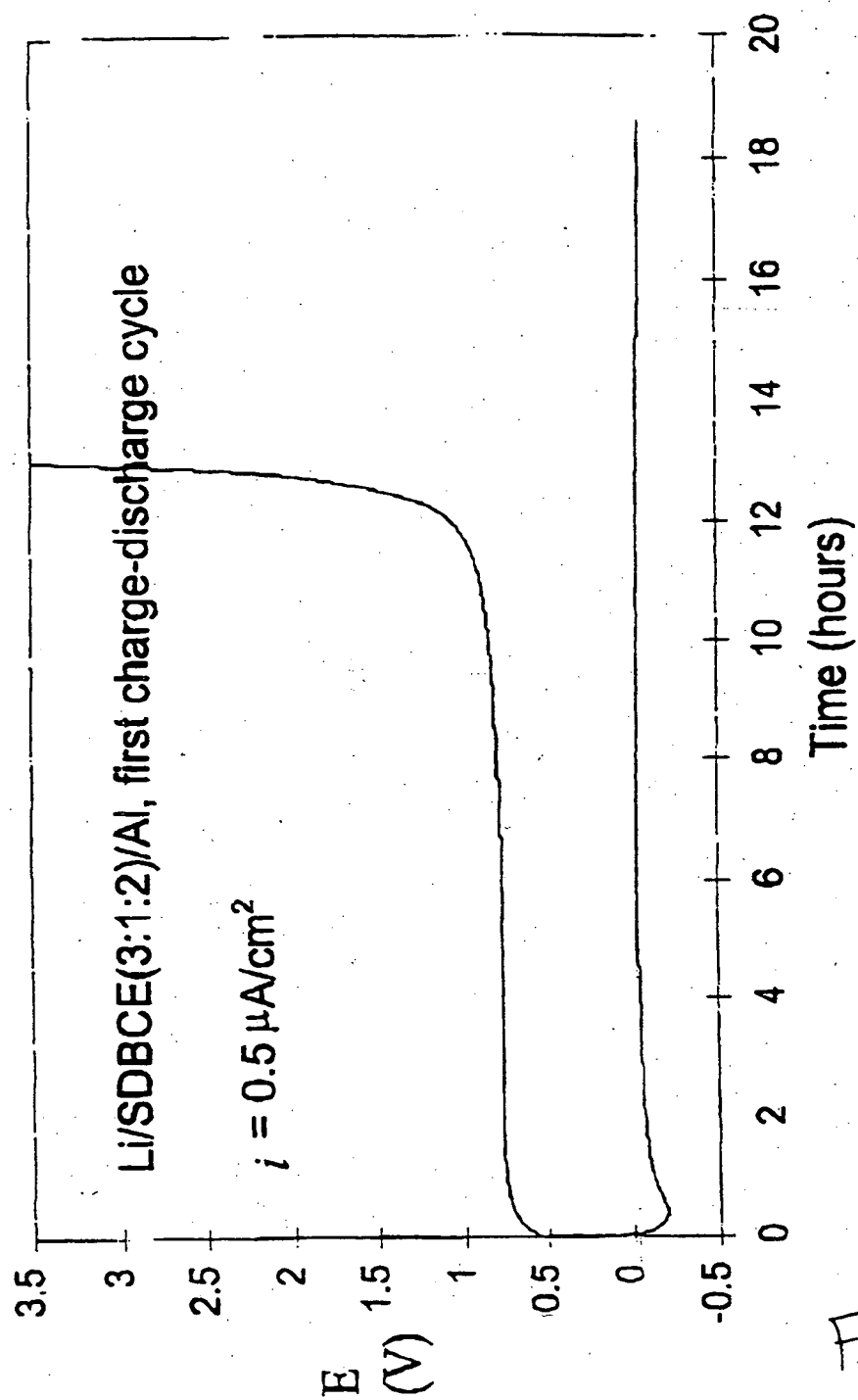


Figure 7

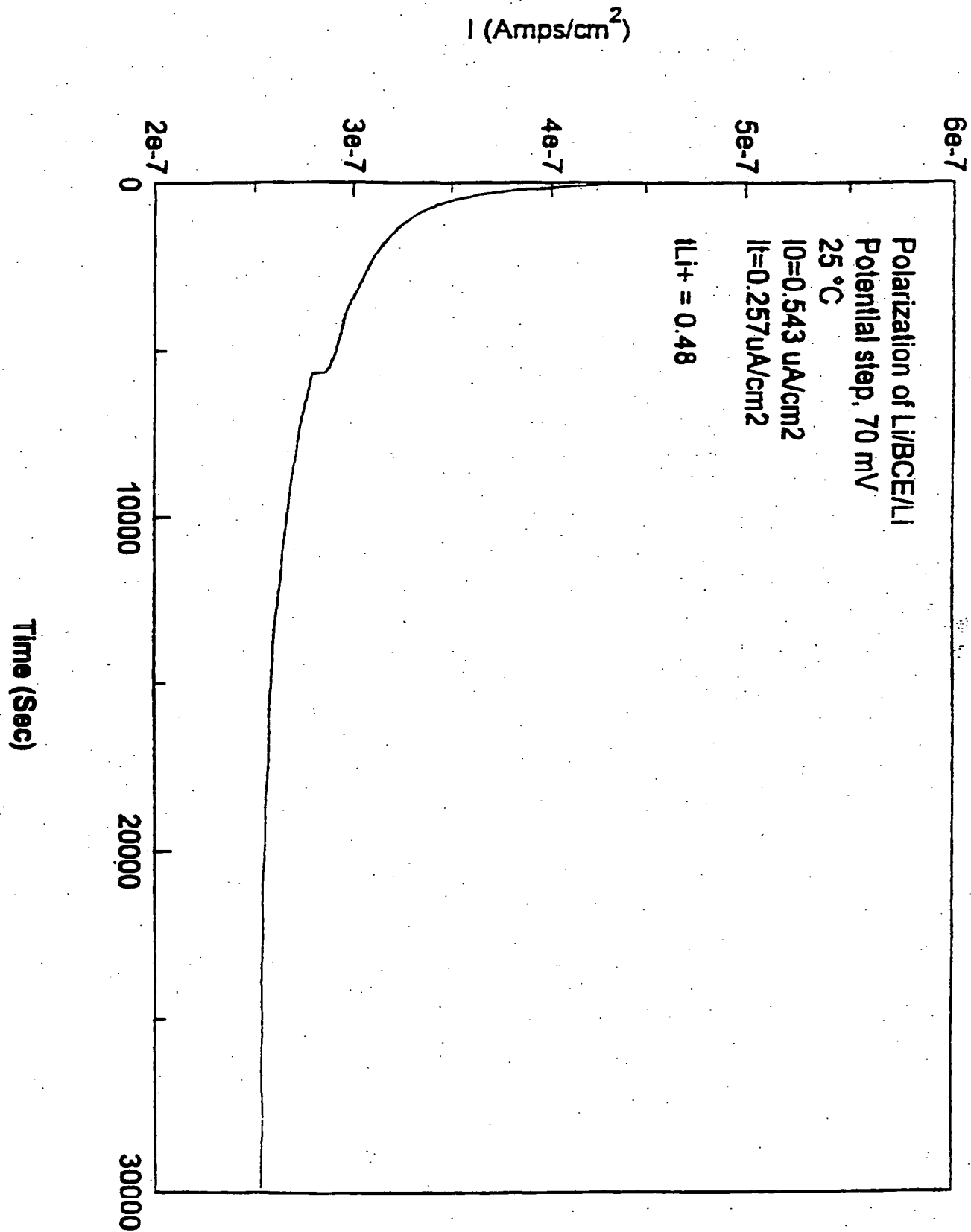


Figure 9

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/16760

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : H01M 6/18, 6/24, 10/08

US CL : 429/ 309, 317, 188

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/ 309, 317, 188

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST 12 (U.S., EPO, JPO), Derwent, NPL

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,102,751 A (NARANG et al) 07 April 1992.	
X	US 5,240,791 A (IZUTI et al) 31 August 1993, col 2, 3, claims 1-12.	1-8, 15-17, 27-34
Y		9-14, 18-26
X	US 5,356,553 A (KONO et al) 18 October 1994, col. 2-4, claims 1-3.	1-8, 15-17, 27-34
Y		9-14, 18-26
Y	US 5,419,984 A (CHALONER-GILL et al.) 30 May 1995, col. 3-6.	1-8, 27-34



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*B* earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A*	document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

14 OCTOBER 1999

Date of mailing of the international search report

04 NOV 1999

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3599

Authorized officer

MARK RUTHKOSKY

Telephone No. (703) 308-0651